Swoner
Pupae

Posts: 99

NaDCCA for hofmann rearrangement of helionamide

Quote

« **on:** May 12, 2020, 12:32:08 AM »

The Hofmann rearrangement has been written about on this forum with TCCA and people have said that it will work with NaDCCA but there were no references. I tried it and it worked extremely well.

3.64g (14.25mmol) of NaDCCA (dihydrate) was dissolved into 250ml of 10% NaOH solution, This took about 30 minutes of stirring to fully dissolve the NaDCCA, It dissolves much easier than TCCA. Once fully dissolved the beaker was placed into an ice water bath and was cooled to 5c. After the solution was cooled down 5.45g of amide was added and stirred until the amide dissolved, this took about 45 minutes. Once everything dissolved the solution was taken out of the ice bath and placed onto the bench to come to RT. Once at RT the beaker was put on max heat on the hotplate. The solution was held at 60c for 10 minutes then brought to 80c and was held for 30 minutes. A white crystal precipitated in the flask that was a byproduct of the NaDCCA. After 30 minutes the heat was removed and the solution was extracted 3x50ml of xylene. The xylene was separated and washed 2x25 with dH2O and 2x25ml of saturated bicarbonate. The xylene was then titrated with dilute HCl until the aqueous layer tested acidic with pH paper. The aqueous phase was reduced with a fan on low heat until there was ~5ml of water left. There was visable crystals forming on the walls of the beaker, 50ml of acetone was poured in and produced a large amount of crystals, The acetone was reduced in front of a fan and the bright white crystals were collected.
Final yield 3.84g (67.3%)

« Last Edit: May 12, 2020, 03:06:39 PM by swoner »

Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

carl

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

Global Moderator
Founding Wasp

Posts: 5,626

circular pastry filled with hazelnut crime

« **Reply #1 on:** May 12, 2020, 01:15:13 AM »

Very good.
I've heard that Na-DCCA is superior too from those who have used it.
You could've used less water though, as thats one of the main advantages over TCCA.

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

Swoner

Pupae

Posts: 99

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #2 on:** May 12, 2020, 01:19:42 AM »

Quote from: carl on May 12, 2020, 01:15:13 AM

> Very good.
> I've heard that Na-DCCA is superior too from those who have used it.
> You could've used less water though, as thats one of the main advantages over TCCA.

This is good to know, The first attempt was done with 200ml of solution in a 250ml beaker but it took far to long to get to temperature, 250ml works very well in a 1000ml beaker though.

Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

loft

Founding Wasp

Posts: 1,154

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #3 on:** May 12, 2020, 07:54:49 AM »

I have little to contribute at this point so I'm just thanking you for finally being one of the few who contributes qualitative experimental content!

Report to moderator Logged

"All things are poison, and nothing is without poison; the dosage alone makes it so a thing is not a poison." - Paracelsus

big mac

5MackO DMT
Founding Wasp

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #4 on:** October 06, 2020, 01:56:23 PM »

I have a question, how are the yields when we perform hypochlorite decarboxylation instead nadcca or tcca? Are they similar or lower?
Hypochlorite is way clearer and more comfy way to go since tcca creates some

Posts: 531

dirt and is poorly soluble and hypochlorite solution is just clear liquid.

Report to moderator Logged

Quote from: Johnathan Ferrous on May 06, 2021, 09:06:39 PM

> Big man, Big Mac.

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #5 on:** October 06, 2020, 02:19:20 PM »

Everything is here...
https://www.thevespiary.org/talk/index.php?topic=2473.0

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

Swoner

Pupae

Posts: 99

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #6 on:** October 06, 2020, 04:19:48 PM »

Quote from: big mac on October 06, 2020, 01:56:23 PM

> I have a question, how are the yields when we perform hypochlorite decarboxylation instead nadcca or tcca? Are they similar or lower? Hypochlorite is way clearer and more comfy way to go since tcca creates some dirt and is poorly soluble and hypochlorite solution is just clear liquid.

From others I have heard that the hypochlorite produces a lot of side reactions and tar, the yields are also no where near as good. Just get NaDCCA, it can be found OTC in its pure form in a certain pool chemical. Ive gotten my yields up to around 75% using a modified method to the one posted here with 20g of amide. I increased the reaction time to 8 hours stirring in the ice bath and 3 hours at 80c. Also I dont know what you mean by decarboxylation, this is a hofmann rearrangement.

« *Last Edit: November 02, 2023, 03:11:32 PM by Sawdust and Honey* » Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

big mac

5MackO DMT
Founding Wasp

Posts: 531

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #7 on:** October 06, 2020, 05:18:33 PM »

Ok hoffmann sounds good too, but it's similar to decarboxylation am I right? Anyways, I'm struggling to dissolve 5g of TCCA in 400ml 10% NaOH for 2nd hour and it doesn't seem to be obey... That's what I wanted to avoid, but if yield is gonna be 20%< I'm gonna try it. Anyways, is it normal for TCCA to be such a big bitch? Does it need to be dissolved completely, forming transparent solution?

Report to moderator Logged

Quote from: Johnathan Ferrous on May 06, 2021, 09:06:39 PM

> Big man, Big Mac.

Swoner

Pupae

Posts: 99

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #8 on:** October 06, 2020, 05:33:41 PM »

Quote from: big mac on October 06, 2020, 05:18:33 PM

> Ok hoffmann sounds good too, but it's similar to decarboxylation am I right?
> Anyways, I'm struggling to dissolve 5g of TCCA in 400ml 10% NaOH for 2nd hour and it doesn't seem to be obey... That's what I wanted to avoid, but if yield is gonna be 20%< I'm gonna try it. Anyways, is it normal for TCCA to be such a big bitch? Does it need to be dissolved completely, forming transparent solution?

Its not too similar to a decarb, I suppose you could make a comparison that they both get rid of a carboxylic croup but the decarb completely removes a carboxylic acid while the hofmann produces a primary amine from a amide that is one carbon shorter. TCCA has a very hard time dissolving. Make sure it is ground as finely as possible, you may have to stir it for a few hours. Thats one of the best advantages of NaDCCA, it is much more soluble.

« *Last Edit: November 02, 2023, 03:11:50 PM by Sawdust and Honey* » Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

big mac

5MackO DMT

Founding Wasp

Posts: 531

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #9 on:** October 06, 2020, 05:40:14 PM »

Oh man, what feature of TCCA makes it such time consuming in terms of dissolution? Poor solubility? but it has to do with amount of substance able to dissolve in solvent not with time that it takes.

Report to moderator Logged

Quote from: Johnathan Ferrous on May 06, 2021, 09:06:39 PM

> Big man, Big Mac.

Swoner

Pupae

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #10 on:** October 06, 2020, 05:45:06 PM »

Quote from: big mac on October 06, 2020, 05:40:14 PM

> Oh man, what feature of TCCA makes it such time consuming in terms of dissolution? Poor solubility? but it has to do with amount of substance able to dissolve in solvent not with time that it takes.

Posts: 99

TCCA is very poorly soluble in water. When its stirring in hydroxide it is turning into a hypochlorite solution. Do you know if your TCCA is pure? certain products containing TCCA are mixtures with other stuff that might effect the solubility. I know of one product that are TCCA pucks which contain other stuff. The NaDCCA you can get at hardware stores is a granular powder which is pure on the MSDS.

« *Last Edit: November 02, 2023, 03:11:55 PM by Sawdust and Honey* » Report to moderator

Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

---

big mac

5MackO DMT
Founding Wasp

Posts: 531

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #11 on:** October 06, 2020, 06:25:31 PM »

I don't even really know, but the only ingredient there is TCCA, there isn't any copper sulfate. I got it as a pool chlorine agent.

Report to moderator Logged

Quote from: Johnathan Ferrous on May 06, 2021, 09:06:39 PM

> Big man, Big Mac.

---

big mac

5MackO DMT
Founding Wasp

Posts: 531

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #12 on:** October 06, 2020, 07:04:00 PM »

It says 99% on the ethiquete and 990mg/g, but it doesn't want to dissolve, when I added it it seemed to dissolve quite quickly, but after like few minuted white suspension was formed which remains till now and doesn't want to dissolve. If I add now my amide, it won't work will it?
It looks like amorphous solid forming clouds after settling to the bottom.

« *Last Edit: November 02, 2023, 03:11:26 PM by Sawdust and Honey* » Report to moderator

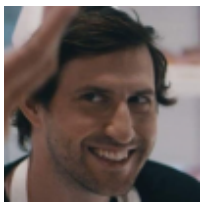
Logged

Quote from: Johnathan Ferrous on May 06, 2021, 09:06:39 PM

> Big man, Big Mac.

Mrbovinejony

Founding Wasp



Posts: 1,413

Seaweed hugger

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #13 on:** October 06, 2020, 08:42:12 PM »

Swoner, maybe it was you I was talking to about this helional method on the other website, but I've always had trouble with it. I think it was mostly due to poor temperature control at the end of the rearrangement. I'm glad you found a method with decent yields because I have too much amide still sitting in jars that need to be used. Have you tried this with bubbling hcl gas into xylene?

Report to moderator Logged

The Germans express it nicely: "Hunger ist der beste Koch,"
which means that a hungry man at table will not complain about quality. - Max Gergel

May all the gods of furious strong be with you as you crunch opponents, and live like a windrammer as you fuck

maker
Subordinate Wasp
Posts: 150

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #14 on:** October 06, 2020, 09:15:28 PM »

I have used sodium hypochlorite 8.25% with the pH brought to 7 or below with acetic acid, to give mostly hypochlorous acid. This was for the Nitrile from phenylalanine. It worked well with not as much crap as you guys seem to have.
The reaction mixture was larger due to the increased water but with an pressure equalized addition funnel to control the rate/ along with an ice water bath, there was no temp problem.

Cleaned fairly easily. No clue if this would work with the helionamide.

« *Last Edit: October 06, 2020, 09:18:01 PM by maker* »

Report to moderator Logged

Swoner
Pupae

Posts: 99

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #15 on:** October 06, 2020, 10:02:18 PM »

Quote from: Mrbovinejony on October 06, 2020, 08:42:12 PM

> Swoner, maybe it was you I was talking to about this helional method on the other website, but I've always had trouble with it. I think it was mostly due to poor temperature control at the end of the rearrangement. I'm glad you found a method with decent yields because I have too much amide still sitting in jars that need to be used. Have you tried this with bubbling hcl gas into xylene?

I've only gassed once and it was a failure from too much suck back, I just titrate with HCl into water and evaporate the water on low heat with a fan and pour in freezer cold acetone to precipitate the salt. I always get beautiful Snow White crystals.

Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

Mrbovinejony
Founding Wasp

Posts: 1,413
Seaweed hugger

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #16 on:** October 07, 2020, 12:06:13 AM »

Did you find a good recrystalization solvent for the amide? I've used ethanol, xylene, and water. All of them give me an oil layer and an aqueous layer. Maybe this means I still have a lot of leftover helional, but some amide makes it into the oil layer and gives me dirty crystals

Report to moderator Logged

The Germans express it nicely: "Hunger ist der beste Koch,"
which means that a hungry man at table will not complain about quality. - Max Gergel

May all the gods of furious strong be with you as you crunch opponents, and live like a windrammer as you fuck

Swoner

Pupae

Posts: 99

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #17 on:** October 07, 2020, 02:22:53 AM »

Xylene and water work well. I also get a dark oil but with water it's easy to separate the two. Boil the water and amide and the brown oil should sink and just decant off the top water into a Pyrex bowl and wash the oil with boiling water again. I think the oil is unreacted helional which can be avoided by increasing the volume of the flask when forming the oxime and using as strong as possible stirring.

Report to moderator Logged

Quote

> Yes I'm paranoid, but am I paranoid enough?

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #18 on:** February 26, 2021, 07:02:44 PM »

What would be a good alternative to xylene for the extraction? Ether? Or maybe DCM, evaporate it off, redissolve the freebase of amine in ether and acidify?

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

carl

Global Moderator
Founding Wasp

Posts: 5,626

circular pastry filled with hazelnut crime

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #19 on:** February 26, 2021, 07:09:13 PM »

All of them work well.

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

aes256

Founding Wasp

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #20 on:** February 27, 2021, 10:41:28 AM »

Posts: 841

DCM is great for quickly evaporating and then taking the freebase up in IPA, acidifying to neutral, then crashing product out with cold anhydrous acetone. But damn it if that DCM doesn't find its way into every little nook and cranny, namely the interface between the stopcock and the sep funnel - I swear it's too good a solvent and manages to leak out of my sep funnel every time! aaarrrggggh

Report to moderator Logged

Quote from: Eleusis

> However, I had serious misgivings about sharing because my quest was one for knowledge and experience while, I knew, for most others it would be for purely economic reasons.

Quote

> He hardly ever spoke of magic, and when he did it was like a history lesson and no one could bear to listen to him.

Quote from: Orange

> you can always dont make things.
> but u cant always make things happen.

aes256

Founding Wasp

Posts: 841

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #21 on:** February 27, 2021, 10:46:12 AM »

I honestly don't know what everyone is doing differently to me regarding dissolving either TCCA/DCCA but I've never, *ever* had trouble dissolving either salt in lukewarm 10% NaOH solution. The chlorine source comes in the form of those big hard pucks, which are pretty hard to break but once shattered into a few pieces the mortar and pestle makes quick work of them (along with ample elbow grease!). Finely powdered, both salts dissolve with ease. I really don't see what the fuss is about!

Report to moderator Logged

Quote from: Eleusis

> However, I had serious misgivings about sharing because my quest was one for knowledge and experience while, I knew, for most others it would be for purely economic reasons.

Quote

> He hardly ever spoke of magic, and when he did it was like a history lesson and no one could bear to listen to him.

Quote from: Orange

> you can always dont make things.
> but u cant always make things happen.

skektek

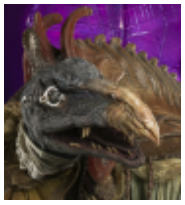
Subordinate Wasp

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #22 on:** February 27, 2021, 11:58:17 AM »

that is probably the key the finely crushed powder.



Posts: 165

Distiller of Gelflings

most TCCA DCCA that I have seen comes in small particles but not fine powder.

I think most just use it as it is.

my sep funnel has no probs with DCM it has a ptfe stop coke and is of the isolab brand.

I find what annoys me about DCM is when you shake your funnel then go to remove the stopper at the top that it wants to spit shit at me.

I know I could probably cool the funnel but I always have too much to do and not enough time.

Report to moderator Logged

GIVE ME ESSENCE

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

« **Reply #23 on:** February 27, 2021, 04:13:01 PM »

Quote

Out of the same amounts as in the original post, 1.2g of fluffy, white MDA HCl crystals were obtained. Some differences during the reaction were observed:
1. NaDCCA dissolved after barely 3 minutes of stirring and formed a clear, lightly yellow-greenish solution. That may be because the NaDCC was ground in a mortar beforehand.
2. The reaction mixture was opaque in every stage of the reaction after adding the amide. At first that was due to undissolved amide, then due to carbon dioxide bubbling steadily, then the white-ish precipitate. At the end of heating, something crashed out and the solution got much more yellow than at the beggining, when it was just barely greenish.

The extraction was done as follows:

The mixture was extracted with total 80ml of DCM (3 portions of 25-30ml). This made all of the visible freebase, reddish oil go into the DCM layer and form a dark yellow, clear phase. Then the DCM extracts were washed once with water. Then to the DCM extracts there was added 25ml of water and the aqueous layer was acidified by dropwise addition of 36% fuming HCl. The aqueous layer was drained out and the DCM was extracted with dilute HCl once again. Then the aqueous portions were basified by dropwise addition of 20% NaOH. First bright white, fine preciptate formed which then converted into oil and sank to the bottom of the beaker. The basified mixture was then extracted with 3 portions of -15C ether. This ether was then dried using anhydrous magnesium sulphate, acidified with conc. HCl and 30ml of ice-cold acetone was added.

I made the rookie mistake of checking the pH of ether layer instead of the aqueous layer, which sank to the bottom and in consequence I overacidified the mixture. 1.2g of MDA HCl was obtained as a light, white solid and it was washed with additional 30ml of acetone.

Photos:
1. Amide used for the reaction
2. small droplets of MDA freebase visible sinking to the bottom of reaction vessel
3. Final product

foto_no_exif (9).jpg (179.61 kB, 2048x2738 - viewed 196 times.)

foto_no_exif (10).jpg (50.89 kB, 720x1280 - viewed 169 times.)

foto_no_exif (11).jpg (181.08 kB, 2738x2048 - viewed 186 times.)

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #24 on:** June 19, 2021, 01:30:55 PM »

As time passes, I acquire experience, my equipment gets better and my patience increases.
Hence I decided to give this method another try.

Chemicals:
7.28g NaDCC dihydrate (~29 mmol)
400ml 10% NaOH
10.90g helionamide (~53 mmol)

Procedure and observations:
The entire 7.28g of sodium dichloroisocyanurate dihydrate was added to 400ml of warm 10% NaOH. I made the mistake of not crushing the little granules into a powder as before. If you're going to attempt this, crush the NaDCC into a fine powder. After nearly an hour of heating there was still a cloud of very fine precipitate visible in the beaker.
Then the helionamide was added in portions (no exotherm was observed, so it would probably be possible to just dump it in).
The mixture was heated to 70C and then to 90C. Total heating time was about 2 hours. The reaction was monitored by TLC on silica (eluent: 7:3 ethyl acetate/hexane, visualized by permanganate. UV works very poorly here in my experience.).

There wasn't much CO_2 evolution - I'd say none, really. Maybe it was all immediately absorbed by the hydroxide and that's why I couldn't see bubbles. TLC was helpful.
A decision was made to hold the RM off-heat, but on stirrer and with a watchglass on top for the entire night (~9h). After letting the mixture stand a thin layer of brown-yellow oil could be seen on coalescing on top. The reaction mixture had a characteristic smell of something trying to smell bad but not doing too good of a job at it 😁. I'd describe it as warm helional that had gone bad.

The reaction mixture was filtered to remove the fine precipitate and the yellow mother liquor was extracted using 3x40ml of DCM. The extracts were red/orange in color. The DCM extracts were extracted using 90ml of water to which 10ml of conc. HCl was added. This mixture was added in 4 portions and the extracts were yellow. This was then basified using first potassium carbonate and then sodium hydroxide. You could as well probably just use sodium hydroxide - the basicity created by the carbonate wasn't enough to fully precipitate the amine freebase.
The mixture was put in fridge and a couple large globules of red oil could be seen on the bottom. The basified mixture was extracted once again with 3x30ml DCM, dried over magnesium sulfate and the DCM was mostly stripped with help of some warm water and a fan.

When the mixture was concentrated to around 20ml it was poured into a 25ml RBF and heated up over a steam bath to draw off any remaining DCM.

Then the oil was vacuum distilled (140C, ~1mbar, remember - first vacuum, then heat! There will be a lot of bumping as some DCM will always remain and has to be first drawn off by the pump - use the gas ballast to remove it from the oil or it will kill your pump). The crude oil weighed 6g and after the distillation it was around 5g. Pure phenylethylamine freebases are colorless - and the distillate was indeed colorless. In the boiling flask there remained red goop that had a smell similar to that of the freebase.

The freebase was taken up in ~20ml of IPA, acidified using 3 pipettefuls of conc. HCl and the salt spontaneously precipitated out as thick crystals after addition of some anhydrous acetone.

The salt was filtered and washed with plenty of acetone. After drying the final yield of very pure (blindingly white!) MDA hydrochloride is around ~50%. The converesion to salt is nearly quantitative, but remember to collect the second crop from the washings (I forgot about it and lost ~500mg of the product).

Attaching photos...

1. Freebase before distillation
2. Freebase after distillation
3. Residue after distillation
4. TLC of the freebase (not too successful, the amine didn't move much in one eluent system I tried)
5. The hydrochloride precipitating out after acetone was added
6. The hydrochloride being dried and filtered
7. The final product

I also have the video of vac. distillation but for safety reasons I'm not going to upload it publicly. If anyone's interested they can hit me up in DMs...

1.jpg (59.85 kB, 1111x326 - viewed 131 times.)

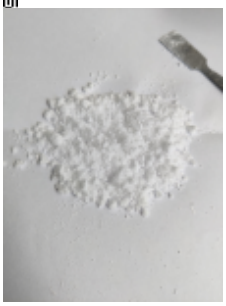
2.jpg (1770.02 kB, 1944x2592 - viewed 126 times.)

3.jpg (691.87 kB, 1895x1337 - viewed 100 times.)

4.jpg (1802.16 kB, 1944x2592 - viewed 169 times.)

5.jpg (1603.13 kB, 1944x2592 - viewed 112 times.)

6-min.jpg (612.79 kB, 3000x4000 - viewed 129 times.)



7-min.jpg (921.33 kB, 3000x4000 - viewed 169 times.)

« *Last Edit: June 19, 2021, 01:37:00 PM by Sawdust and Honey* » Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

carl
Global Moderator
Founding Wasp

Posts: 5,626

circular pastry filled with hazelnut crime

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #25 on:** June 19, 2021, 10:02:59 PM »

Huh, nobody said anything the first time, so I'll just do it for both posts: they are great stuff!
Thank you for posting this!

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

Mrbovinejony
Founding Wasp

Posts: 1,413

Seaweed hugger

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #26 on:** June 20, 2021, 12:14:21 AM »

I thank you as well! I've been planning on redistricting my mda since it's been sitting for a while and turning brown, its good to know that you had no trouble with it

Report to moderator Logged

The Germans express it nicely: "Hunger ist der beste Koch,"
which means that a hungry man at table will not complain about quality. - Max Gergel

May all the gods of furious strong be with you as you crunch opponents, and live like a windrammer as you fuck

RhinoJackson
Subordinate Wasp

Posts: 109

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #27 on:** June 20, 2021, 01:26:12 AM »

Excellent posts! Love the TLC!

Report to moderator Logged

loft
Founding Wasp

Posts: 1,154

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #28 on:** June 21, 2021, 08:36:21 AM »

Quote from: carl on June 19, 2021, 10:02:59 PM

Huh, nobody said anything the first time, so I'll just do it for both posts: they are great stuff! Thank you for posting this!

I was just wondering about the same thing: why did no one comment on the first great post?
Either way: thank you for sharing your detailed and high quality results!

Is NaDCCA better than TCCA in this reaction?

Report to moderator Logged

"All things are poison, and nothing is without poison; the dosage alone makes it so a thing is not a poison." - Paracelsus

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #29 on:** June 21, 2021, 09:03:46 AM »

Yes, absolutely. There is no reason to use TCCA in my experience. It's not really a case of reactivity, more of solubility. The reaction can be indeed very facile (as described by Swoner in the original procedure) if all of the chlorine source is dissolved.
The MDA was bioassayed with interesting results... not on me, but two of my friends had a distinctly different trip. One was calm and sensual while the other one started climbing wooden sheds .

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

Mustacho

Subordinate Wasp

Posts: 161

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #30 on:** July 04, 2021, 04:33:16 PM »

Very interesting, good posts.

So its important to grind the TCCA/NaDCCA down finely for it to dissolve more easily.
The TCCA found in the pool products i found seem to have a minor amount, 2.5-5% Boric acid added, does this interfere with the reaction or cause problems?
Maybe other brands that is pure TCCA can be found, i just checked a few.
The NaDCCA pool variant seem to be pure, at least the MSDS doesnt show any other chemical.
Both variants seem to be commonly available and cheap too :-)

Report to moderator Logged

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #31 on:** July 04, 2021, 04:38:24 PM »

Boric acid doesn't influence the reaction in any way. Sometimes copper or aluminium salts are added as well, I doubt they do anything either. They just precipitate out as the hydroxide or redissolve as the hydroxide complex. Use the sodium salt if possible, it's simply more convenient.

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

Mustacho
Subordinate Wasp
Posts: 161

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #32 on:** July 05, 2021, 08:18:27 PM »

I want to try the NaDCCA hofmann rearrangement but i need to make the helionamide first and i have no 30% H2O2.
There must be other ways to make the amide, i will search for an alternative procedure.

I try the Helional -> aldoxime -> amide from two dogz using hydroxylamine and nickel acetate.
Then i can try the NaDCCA in this thread.

« Last Edit: July 05, 2021, 08:53:18 PM by Mustacho »

Report to moderator Logged

Sawdust and Honey
Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #33 on:** July 05, 2021, 08:54:53 PM »

Well, the nitrile formed can be oxidized to an amide in a hundred different ways. Why not isolate the nitrile and then oxidize it with acetic acid/sulfuric acid system?
hx tps://pubs.acs.org/doi/10.1021/jo048240a

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

carl
Global Moderator
Founding Wasp

Posts: 5,626

circular pastry filled with hazelnut crime

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #34 on:** July 05, 2021, 08:58:47 PM »

Just search and don't ask to be spoonfed, there are several different ways to get to this amide and most of the accessible ways are documented on here.

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

Mustacho
Subordinate Wasp
Posts: 161

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #35 on:** July 06, 2021, 08:02:46 AM »

Sorry, i didnt mean to be lazy and i have searched but maybe i searched for the wrong keywords.
Im not so well educated in chemistry but im trying to learn.
I try search better until i find a somewhat easy way using chemicals and procedures i can do.

Report to moderator Logged

ketosis
Just some bee
Dominant Wasp
Posts: 410

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #36 on:** July 23, 2021, 05:59:02 AM »

Quote from: maker on October 06, 2020, 09:15:28 PM

> I have used sodium hypochlorite 8.25% with the pH brought to 7 or below with acetic acid, to give mostly hypochlorous acid. This was for the Nitrile from phenylalanine. It worked well with not as much crap as you guys seem to have.
> The reaction mixture was larger due to the increased water but with an pressure equalized addition funnel to control the rate/ along with an ice water bath, there was no temp problem.
>
> Cleaned fairly easily. No clue if this would work with the helionamide.

This.

zoom -he flies off into research

@Sawdust/Honey = Fabulous report!
Carl: Maybe with some edits, this can go to published section?

I have lab grade TCCA, kinda pricey, but thought i'd eliminate one more unknown while still noobin'

Report to moderator Logged

carl
Global Moderator
Founding Wasp

Posts: 5,626
circular pastry filled with hazelnut crime

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #37 on:** July 23, 2021, 08:37:45 AM »

Quote from: ketosis on July 23, 2021, 05:59:02 AM

> Carl: Maybe with some edits, this can go to published section?

Sure!

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

sparklebags
Dominant Wasp
Posts: 457

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #38 on:** October 02, 2021, 11:14:03 PM »

I am about to try a NaDCCA Hofmann. I noticed that Carl mentioned the amount of water could be reduced, it appears most of the trials were more dilute or around the same dilution as the original write up (I think it was around 40g amide/14g TCCA/ 1L NaOH solution). It could be significantly more concentrated with the NaDCCA correct? Would simply finding the solubility of NaDCCA and amide in a base solution be enough to determine how much so?

Report to moderator Logged

carl

Global Moderator
Founding Wasp

Posts: 5,626

circular pastry filled with hazelnut crime

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #39 on:** October 03, 2021, 03:36:51 AM »

Why do you need the solubility of the amide?
Is that even known?
Do you not add your amide dissolved in dioxane?
This helps to reduce the volume even further

Yeah maybe do some experiments regarding the solubility if you want to?

Report to moderator Logged

Quote from: Moriarty on September 08, 2015, 05:10:02 AM

> I would suggest that you guys share information like it was the last day on Earth. This information slowdown is all because of all that dumb unwillingness to share. That is where the DEA is winning. There goal is you not talking to each other. Let the information flow. I promise we will always be 2 steps ahead of DEA chemists if we just keep sharing information

Quote

> Real bees just hear the buzzing and it doesn´t ever stop. Ever.

sparklebags

Dominant Wasp

Posts: 457

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #40 on:** October 19, 2021, 01:15:39 PM »

Yeaaaaaah.....I was going to mess with figuring out the amide with NaDCCA solubility vs with TCCA but I got lazy and just increased the concentration by 30%. Made the NaOH solution, added NaDCCA, cooled to 15* added amide, slight increase in temp (22* but over time as the ice melted), I let it run overnight in an ice bath, in the morning I noticed a layer of shimmering glittery amide looking foam on top. I moved it to a larger vessel and added more water, it quickly went into solution. Unlike with TCCA however it is somewhat clear reddish - I may have just diluted the crap out of it.

Report to moderator Logged

sparklebags

Dominant Wasp

Posts: 457

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #41 on:** October 22, 2021, 01:26:18 PM »

I just finished this run, the DCCA is far superior - in my opinion - than TCCA. Breaking those pucks up, particularly at any scale, is a giant annoyance. I just poured the DCCA granules in the warm NaOH. I did find that I wasn't able to really use much less NaOH solution, but this wasn't exactly a controlled run. More importantly, the end product after gassing was noticeably cleaner and required less work to get it nice and white. I did have fairly MSM free amide, but that's not unusual. Kudos! Oh yeah, right around 70% yield with one mess up, so could have easily been 75-80%.

Report to moderator Logged

aes256

Founding Wasp

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

Posts: 841

« **Reply #42 on:** October 22, 2021, 03:02:44 PM »

I never really understood people's frustration with getting TCCA to dissolve. I always broke the pucks apart and powdered them in a mortar and pestle and dissolved the very fine powder in freezing cold 10% NaOH with good stirring or shaking. Never had any problems getting it to dissolve.

Report to moderator Logged

Quote from: Eleusis

> However, I had serious misgivings about sharing because my quest was one for knowledge and experience while, I knew, for most others it would be for purely economic reasons.

Quote

> He hardly ever spoke of magic, and when he did it was like a history lesson and no one could bear to listen to him.

Quote from: Orange

> you can always dont make things.
> but u cant always make things happen.

dolittle

Larvae

Posts: 11

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #43 on:** May 13, 2023, 04:26:46 PM »

is it possible to just use a blender/coffee grinder to pulverize TCCA pucks? assuming you can even find real tcca pucks anymore. We are sick and tired of making/purifying perfect looking amide only to piss it away with a sodium hypochlorite hoffmann. We want that TCCA grade MDA! And thank you to whomever recommended an actual blender for mixing the bleach lye amide hoffmann reaction, results are definitely better looking with less unreacted solids at the end, once the solvent has dissolved the mda and floated to the top, the aqueous layer is clear

Report to moderator Logged

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #44 on:** May 13, 2023, 04:29:00 PM »

Or just buy granulated pool disinfectant with NaDCCA or TCCA in the MSDS..?

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

dolittle

Larvae

Posts: 11

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #45 on:** May 13, 2023, 05:13:07 PM »

Ill try that. Whatever else if anything besides DCCA is in the granules is hopefully inactive if its not soluble/wont interfere with the reaction, but filtering it out is an option too. The worst that can happen is I waste a little amide which is nothing new for me haha. Simply i have an irrational fear of

using anything from the hardware store in synthesis (besides xylene for extraction or acetone for cleaning glass) But yeah, we want an improvement on the hypochlorite hoffmann. thank you.

Report to moderator Logged

Sawdust and Honey

Founding Wasp

Posts: 1,610

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #46 on:** May 13, 2023, 05:15:40 PM »

Sometimes a bit of aluminum hydroxide, copper sulfate or boric acid/sodium borate is added but none of them are an issue.

Report to moderator Logged

End of the road. Nothing to do, no hope of things getting better.
Sounds like Saturday night at my house.

dolittle

Larvae

Posts: 11

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #47 on:** June 15, 2023, 12:54:42 AM »

we tried the DCCA hofmann, its sold as a different name for DCCA. It worked! following the original post, we got slightly more than 50% yield which is a lot better than most of the hypochlorite hoffmanns we have done. The freebase comes out much lighter, as does the dried crystals which i usually have to do several washes/ rextal before it comes anything close to this. And the experience consuming it is more potent, better visuals, and much more relaxed i think, but we only tasted 30-40 mg. Thank you guys. Stable chlorine sources sold in solid forms are the way to go here, no guessing and praying that the hypochlorite you bought isnt already too old or contaminated, we lost so much amide just because of that. Oh also, if you like almost zero tar and crap during extraction and workup DCCA is your best friend cause there was so little tar i thought something was wrong lol. Whether or not this is scalable is irrelevant cause it makes better MDA.

Report to moderator Logged

Fable

Larvae

Posts: 20

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #48 on:** June 15, 2023, 01:29:43 AM »

Take this with a grain of salt if you will but this was my first run on the hofmann.

A 2.5 mol/L NaOH solution was prepared (25g in 250ml H2O) and chilled to 5 deg in the fridge.
50mmol of amide (10.3g) was added to the 10% NaOH solution. (Amide 207 g/mol) (Amide will not dissolve, don't be concerned)
A 25mmol solution of NaDCC was prepared (6.4g in 25 ml of H2O) and chill to 5 deg in fridge. (NaDCC 256 g/mol). This solution solidifies at prolonged fridge temperatures, warm to liquid before mixing.
The solutions were combined in a 500ml flask and stirred for a minimum of 6-8 hours while keeping at 5 deg c. In practice, the cooling/stirring will sit overnight in the ice bath so the time is more like 14 hours.
Cooling and stirring are achieved by placing a large plastic bowl on the stir plate, setting the flask in the bowl, and filling the bowl with ice, some salt, and a small amount of water.

After the required time, the flask was removed from cooling and the cyanuric acid precipitate was filtered. The solution (275ml) was retained and the solids were discarded.

A 2.5 mol/L NaOH solution (12.5g in 125ml) was prepared and heated to 85 deg c.
The previously filtered solution (275ml) was added in 25ml portions to the hot NaOH solution every 10 minutes with continual stirring, this takes 110 minutes.
Once complete, the reaction was maintained at 85 deg c for 2 hours.
Following the 2 hour period, the flask was remove from the heat and let sit overnight.
The resultant solution was extracted with (DCM) organic solvent 3 times.

Vacuum distil to recover the solvent, titrate with HCL into water & evaporate the water.

Yield 80%

Wash with dry acetone to clean up if necessary.

Report to moderator Logged

aes256
Founding Wasp

Posts: 841

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #49 on:** June 16, 2023, 05:15:14 PM »

@Fable do you have any photos of your finished product? 80% yield is molar percentage yeah?

Report to moderator Logged

Quote from: Eleusis

> However, I had serious misgivings about sharing because my quest was one for knowledge and experience while, I knew, for most others it would be for purely economic reasons.

Quote

> He hardly ever spoke of magic, and when he did it was like a history lesson and no one could bear to listen to him.

Quote from: Orange

> you can always dont make things.
> but u cant always make things happen.

Fable
Larvae

Posts: 20

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #50 on:** June 17, 2023, 03:03:43 AM »

Sure thing.
FYI the procedure above was put together prior to running the experiment, at the time I didn't have 10.3g of amide available, so I used roughly 9g and adjusted the molar ratios for that.

IMG2Hoff - .jpg (318.79 kB, 748x998 - viewed 126 times.)

Report to moderator Logged

Fable

Larvae

Posts: 20

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #51 on:** August 18, 2023, 01:13:06 AM »

I reran the procedure with 10.3g of amide, I ended up using slightly more water to dissolve the NaDCC, and after washing all the glassware to get all the remnants, I ended up with a total volume of around 325ml.
Everything ran smoothly until I decided to try to vac distil the freebase. I added some d-limonene so as not to heat the freebase to dryness and I just couldn't get the mixture hot enough or pull a large enough vacuum to bring anything over. My hotplate max temp was set at 228 Deg C, so I need to disengage the safety endpoint as it can get up to 310 or so, time to find the manual.
After the mixture cooled I added an estimated molar equivalent of HCl and a dash of DCM which was probably unnecessary and also caused an emulsion.
After recovery and desiccation the crude yield was 9.0g, so a molar yield of 83.85%
The colour was a darker hue than before which I put down to exposing the freebase to the heat of the failed vac distil.
Next plan is a cold acetone wash followed by a recrystallisation.

Report to moderator Logged

dolittle

Larvae

Posts: 11

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #52 on:** December 31, 2023, 03:27:06 PM »

I tried running the first part with nitrile derived amide, it stayed at or below 5c for the first 2-3 hours at least before i gave up trying to keep it at 5c and just set it in ice cold water while it stirred for several more hours. Filtered the solution and a bit of what looks like nitrile etc was filtered out. Then pouring it incrementally into 85c base on a RB mantle, we decided to just add it incrementally until it was 80c before pausing and letting temp climb to 85 again, then heated at 85 for another 2 hours then added toluene. Temp got as high as 92c during heating. At 2 hours heating some solids were in the reaction which were not present before, 1-2 hours more heating and these solids all disappeared. The freebase in toluene looks like the right color. I probably didn't need to rush through adding the reaction to the hot base but impatient, still need to run heat for 4+ hours for best results maybe. What are those solids seen during heating? And during the first part at 5c, is it ok if temps are below 5c? And does the amide go bad over time? I was told this amide can last for many years.

we also tried it with beckmann derived amide all just in a beaker on a hotplate, just let it stir at room temp overnight, everything dissolved and

solution wasnt filtered, then just heated the flask to 85c during the heating lots of solids crashed out which wouldnt redissolve, forgot heating time and maybe wasnt heated long enough or we didnt use enough base, by the time we stopped there was still tons of very white solids still in the reaction that did not dissolve in toluene or the basic reaction, but when filtered from the reaction those solids will dissolve fast in regular distilled water. Extraction with solvent looks weak. Either way fun to play around with this a bit.

Report to moderator Logged

sparklebags
Dominant Wasp
Posts: 457

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #53 on:** November 17, 2024, 06:04:40 AM »

I ran another NaDCC reaction and noticed the same thing as last time; the final salt looks very different than when I have ran it with TCCA. It is more powder like vs with TCCA I get more of a granular crystal like product. Has anyone else noticed this?

Report to moderator Logged

IA_Wales
Larvae
Posts: 11

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #54 on:** December 04, 2024, 02:24:01 AM »

> **Quote from: sparklebags on November 17, 2024, 06:04:40 AM**
>
> I ran another NaDCC reaction and noticed the same thing as last time; the final salt looks very different than when I have ran it with TCCA. It is more powder like vs with TCCA I get more of a granular crystal like product. Has anyone else noticed this?

Do you have the same workup conditions? I have always gotten pretty large crystals when slowly evaporating from an acidic solution with the help of some IPA.

Report to moderator Logged

cactus-boofer
Subordinate Wasp
Posts: 129

Re: NaDCCA for hofmann rearrangement of helionamide

Quote

« **Reply #55 on:** December 08, 2024, 01:21:05 AM »

Why no TLC porn in this thread yet?

Report to moderator Logged

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